

**CONCEPTUAL DESIGN OF 5 KG/HR PRODUCTION OF
PENTAERYTHRITOL TETRADODECANOATE (PETD)**

JEDIDIAH JOHNNY

**A thesis submitted in fulfillment of the requirements for the award of the
degree
of Bachelor of Chemical Engineering**

**Faculty of Chemical & Natural Resources Engineering
University College of Engineering & Technology Malaysia**

NOVEMBER 2006

I declare that this thesis entitled “*Conceptual Design of 5 kg/hr Production of Pentaerythritol Tetradodecanoate (PETD)*” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature :

Name of Candidate : JEDIDIAH JOHNNY

Date : 20 NOVEMBER 2006

Special Dedication to my...

Beloved parents;
Johnny Lagang Tapan
Julie ak Edward

Beloved sister;
Jacobina Johnny

Encouraging friends;
Shahril Mohamad
Azrul Azmi Yaziz
Mohd Farridd Termizi

For Their Love, Support, Advices, Help and Best Wishes.

ACKNOWLEDGEMENT

I would like to take this opportunity to express my gratitude to my beloved father and mother, Johnny Lagang Tapan and Julie ak Edward. I am grateful to have both of you in my life and giving me full of support to through this life. I pray and wish to both of you are always in a good health. You are the most precious gift me.

I am indebted to my supervisor, Sir Mohd Sabri bin Mahmud the lecture from the Faculty of Chemical Engineering and Natural Resources for his advice, insightful comments and generous support. Thank you for your guide and without your guide this research will not complete and well organized. I also want to thank you for your support and brilliant ideas that you gave me.

I would like to dedicate my appreciation to all the lecturers that involve in this subject/project for their invaluable time, guidance and advice. Without your cooperation and sacrifices this research will not able to complete and published.

Not forgotten to all my beloved sister and encouraging friends who have accompanied me through this project. To my sister Jacobina Johnny, and my friends Shahril Mohamad, Azrul Azmi Yaziz and Mohd Farridd Ahmad Termizi who gave me moral support and be patient throughout this year therefore give me strength, ideas and encouragement. Thank you very much.

ABSTRACT

Conceptual design is becoming a common method used in the industries to estimate and design the optimum condition for their production, by concerning the time and money constraint. The objective of this study is to synthesis the process flowsheet for the optimum production of Pentaerythritol Tetradodecanoate (PETD) at 5 kg/hour. This study covers on the production cost estimation. The analytical methods of finding the properties were done using Thermogravimetry Analysis (TGA), Differential Scanning Calorimeter (DSC) and Calorimeter Bomb. To validate the conceptual design, rigorous steady state simulations are performed. Extensive simulation using ASPEN Plus software was performed and a scheme that can address the requirement is proposed. This study shows the usage of concepts to model the optimum design of reaction, separation and the utilities of PETD production. The framework which used to develop the flowsheet scheme is general enough for further investigation by extending its application to other problem.

ABSTRAK

Reka bentuk konsep telah menjadi satu kaedah lazim yang digunakan oleh industri untuk menganggar dan mereka bentuk keadaan optimum bagi pengeluaran mereka dengan mengambil kira kekangan masa dan kewangan. Tujuan bagi kajian ini ialah untuk mensintesis rajah alir proses yang optimum bagi penghasilan “Pentaerythritol Tetradodecanoate (PETD)” pada kadar 5 kg/jam. Kajian ini meliputi anggaran kos pengeluaran. Kaedah analitikal untuk mencari sifat-sifat kimia dilakukan dengan menggunakan “Thermogravimetry Analysis (TGA)”, “Differential Scanning Calorimeter (DSC)” and Kalorimeter Bom. Untuk mengesahkan reka bentuk ini, satu simulasi keadaan stabil yang menghampiri proses sebenar dilakukan. Simulasi dilakukan menggunakan perisian ASPEN Plus dan satu skema untuk menepati keperluan telah dicadangkan. Kajian ini menunjukkan penggunaan konsep untuk pemodelan keadaan reka bentuk optimum bagi tindak balas, pemisahan dan utiliti dalam penghasilan PETD. Struktur yang digunakan untuk menghasilkan rajah alir adalah sangat lazim untuk kajian seterusnya dengan aplikasi kepada masalah yang lain.

TABLES OF CONTENTS

CHAPTER	TITLE	PAGE
	DECLARATION	i
	DEDICATION	v
	ACKNOWLEDGEMENT	vi
	ABSTRACT (ENGLISH)	vii
	ABSTRAK (BAHASA MELAYU)	viii
	TABLE OF CONTENT	ix
	LIST OF TABLE	xii
	LIST OF FIGURE	xiii
	LIST OF APPENDICES	xiv
1	INTRODUCTION	1
	1.0 Introduction	1
	1.1 Problem Statement	2
	1.2 Objectives	3
	1.3 Scope of Study	3
2	LITERATURE RIVIEW	4
	2.1 Conceptual Design	4
	2.2 Definition of Terms	5
	2.2.1 Batch Process	5
	2.2.2 Continuous Process	5
	2.2.3 Order-of-magnitude Estimate	5
	2.2.4 Rules of Thumb	6
	2.3 Description of Materials	6
	2.3.1 Raw Material	6

	2.3.2 Product	7
2.4	Chemical Properties of PETD	8
	2.4.1 Thermal Stability	8
	2.4.2 Melting Point	9
	2.4.3 Product Purity	9
	2.4.4 Heat Capacity	10
	2.4.5 Enthalpy	10
	2.4.6 Heat of Combustion	11
2.5	Simulation	13
3	METHODOLOGY	14
3.1	Design of Process Flowsheet	14
	3.1.1 Batch versus Continuous	15
	3.1.2 Input-Output Structure	15
	3.1.3 Recycle Structure of the Flowsheet	16
	3.1.4 Separation System	16
	3.1.4.1 Relative Volatility	17
	3.1.4.2 Minimum reflux	17
	3.1.4.3 Minimum stages	18
	3.1.5 Heat-Exchanger Network	18
3.2	Analytical Method	19
	3.2.1 Analysis Using TGA	19
	3.2.2 Analysis Using DSC	20
	3.2.3 Analysis Using Bomb Calorimeter	20
3.3	Cost Study	21
3.4	Simulation assumption	21

4	RESULTS AND DISCUSSION	23
4.1	Process Flow Diagram	23
4.2	Analytical Result	24
4.2.1	TGA	24
4.2.2	DSC	26
4.2.3	Calorimeter Bomb	29
4.3	Hierarchy of Decision	
4.3.1	Level 0: Input Information	29
4.3.2	Level 1: Batch versus Continuous	30
4.3.3	Level 2: Input-Output Structure	30
4.3.4	Level 3: Recycle Structure of the Flowsheet	31
4.3.5	Level 4: Separation System	31
4.3.6	Level 5: Heat Exchanger Network	32
4.4	ASPEN Plus Simulation	32
4.5	Chemical properties estimation	33
4.6	Production Cost	34
5	CONCLUSION AND RECOMMENDATIONS	35
5.1	Conclusion	35
5.2	Recommendations	36
	REFERENCES	37
	APPENDICES	39

LIST OF TABLES

TABLE NO.	TITLE	PAGE
2.1	Raw material properties (Sources: Adapted from http://www.sciencelab.com)	7
2.2	Physical properties of PETD	8
3.1	Process simulation parameters (Sources: Adapted From Q. Smejkal, M.Soos, 2001)	21
4.1	Percentage of PETD and decomposition point	24
4.2	Observation of melting	26
4.3	Temperature Rise in Calorimeter Bomb	29
4.4	Component destination	31
4.5	Stream cost	32
4.6	Simulation Stream Result	33
4.5	PETD Pure Component Properties	33

LIST OF FIGURE

FIGURE NO.	TITLE	PAGE
3.1	Flow sheet of the equilibrium reactor and the distillation column for production of PETD. (Sources: Q. Smejkal, M. Soos, 2001)	22
4.1	Process Flow Diagram (PFD)	23
4.2	Weight Percentage versus Temperature (Overall TGA analysis plot)	25
4.3	Heat Flow versus Temperature (Overall DSC analysis plot)	27
4.4	Temperature rise profile (Calorimeter bomb result)	30
4.5	Simulation Flowsheet Diagram	32

LIST OF APPENDICES

APPENDIX.	TITLE	PAGE
Appendix A.1	Plot of TGA analysis	39
Appendix A.2	Plot of DSC analysis	44
Appendix B.1	Sizing and costing for reactor	49
Appendix B.2	Sizing and costing for distillation column	50
Appendix C.1	Reactor simulation result	53
Appendix C.2	Distillation column simulation result	54
Appendix C.3	Utilities simulation result	55
Appendix D.1	Cost evaluation	56

CHAPTER 1

INTRODUCTION

1.0 Introduction

Over the past number of years, industry has needed to become more effective in bringing new products to the market. In terms of product design, the effect has been that manufacturers must have extremely efficient product development process [17]. In chemical engineering, we might try to generate new ideas to produce something new or to improve the production with new technologies. These new ideas will be translated into real equipment and processes for producing those new materials or for significantly upgrading the value off those existing products.

While conceptual design is regarded as the most demanding phase of design on the designer [14], it also offers the greatest scope for improvements in the design of the product [12]. The design should be done carefully because it affects the accuracy of the estimation cost for designing and operating. All this is called a process synthesis of producing new product where the goal is to find the best process flow sheet and estimating the optimum design condition [1]. It is widely acknowledge that up to 80 per cent of a product's total cost is dictated by decisions made during the conceptual phase of design [14].

For the conceptual design of Pentaerythritol Tetradodecanoate (PETD) production, it is synthesis process of a plant that can produce PETD at optimum rate. This will consider the cost factor as the parameter. The design will be developed by using order-of-magnitude, means that limiting our attention to the major piece of process equipment and then add up the minor piece equipment. At the end of the

project, the best design for the production of PETD will be chosen from the most profitable with a low operating cost and considering all the other factors, including safety and environment control.

1.1 Problem Statement

Traditionally, the design process involves the draftspersons and the design engineers, who, once they have completed their jobs, usually present the blueprints (layouts) of the product to the manufacturing or production division. Product performance failure is usually due to a lack of analysis [18].

The conventional design process may take a lot of time and become costly to be done. From the manual design procedure until the realization of the production, some of the design may not be effective and run as what people want. The manual design procedures that take place is by creating a lot of alternatives, and doing a lot of experiments just for one processes. The process will use a lot of the cost because of damages on the equipments, raw materials, and energy used. Most errors in design, as opposed to those made during production, are due to use of a flawed conceptual design [16].

In this research, the design process that is studied is the conceptual design of Pentaerythritol Tetradodecanoate(PETD) production. Problem that occurs is how to produce the product wanted at an optimum output in terms of purity, production rate, energy consumption and process minimization. Besides, less than 1% of ideas for new designs ever become commercialized [1].

1.2 Objective

The objective of doing this project is to find the process flow diagram and estimate the optimum design to produce 5 kilogram per hour of Pentaerythritol Tetradodecanoate (PETD).

1.3 Scope of Study

This project will cover on the study of the process parameter (ie. chemical and phase equilibrium, entrainer selection, kinetic design and optimization) of the esterification reaction that will affect the operation cost of the plant from the feed of raw material until the final product. The scope of this research is to:

- i. Run an analysis of PETD by using Calorimeter Bomb to find the enthalpy of combustion.
- ii. Find the properties of PETD by using Thermogravimetry Analysis (TGA) & Differential Scanning Calorimeter (DSC).
- iii. Study on the operation cost which involves the number of equipments and materials used in process.
- iv. Run the process simulation by using ASPEN PLUS software.

CHAPTER 2

LITERATURE REVIEW

2.1 Conceptual Design

Generally, concept gives the meaning of a principle or an idea. It also is an abstract, notion or unit that serves to designate a category of entities, events or relations [5]. Conceptual design also has been defined as that phase of design which takes a statement of a design problem and generates broad solution to it in the form of, what are generally referred to as, 'schemes' [12]. Conceptual design is also the process by which the design is initiated, carried to the point of creating a number of possible solutions, narrowed down to single best concepts. It is sometimes called the feasible study [13].

Before this, designs were done empirically. There was no concept practised on designation process. Empirically means that the designation is only based on try and error. A chemist might discover a new reaction to make an existing product or a new catalyst for an existing, commercial reaction, and designers want to translate these discoveries to a new process. Thus, designers start with only knowledge of reaction conditions that they obtain from the chemist, as well as some information about raw materials and product obtained from marketing organization. A lot of these process alternatives to be done to archive the same goal which can be up to 10^4 until 10^9 processes [1].

2.2 Definition of Terms

2.2.1 Batch Process

Batch process refers to a discontinuous process involving the bulk movement of material through sequential manufacturing steps. Mass, temperature, concentration, and other properties of a system vary with time. Addition of raw material and withdrawal of product do not typically occur simultaneously in a batch process.

2.2.2 Continuous Process

Continuous process means a process where the inputs and outputs flow continuously throughout the duration of the process. Continuous processes are typically steady-state.

2.2.3 Order-of-magnitude Estimate

For a beginner designer, it is useful to have a systematic approach for developing order-of-magnitude estimates. Order-of-magnitude estimates usually made before the facility is designed, and must therefore rely on the cost data of similar facilities built in the past [1]. The Order of Magnitude estimate is completed when only minimal information is available. The proposed use and size of the planned structure should be known and may be the only requirement. The “units” can be very general and need not be well defined. The probable accuracy of the design may exceed $\pm 40\%$.

2.2.4 Rules of Thumb

Originally rules of thumb or also known as heuristics evaluations were developed by experienced designers. It is desirable to recover more than 99% of valuable components in column [1].

Heuristic Evaluation is a method of design evaluation. Based on a heuristic evaluation, the expert should also be able to provide alternative design solutions to address potentially major problems for users. The basic approach requires that a domain expert (someone very familiar with product area) review the product design using a set of heuristics (guiding principles e.g. provide appropriate feedback) with the purpose of identifying design decisions (e.g. layout, labeling, etc) that may lead to user errors [8].

2.3 Description of Material

The materials being used for this study are mercury in Pentaerythritol Tetradodecanoate (PETD), Lauric Acid and Pentaerythritol.

2.3.1 Raw Material

Below are some descriptions of the raw materials used in the production of PETD:

Table 2.1: Raw material properties (*Taken from MSDS of material*)

Description	Materials	
	Pentaerythritol	Dodecanoic Acid
Commercial name	-	Lauric Acid
CAS number	115-77-5	143-07-7
Molecular formula	C ₅ H ₁₂ O ₄	C ₁₁ H ₂₂ COOH

Melting point (K)	533.15	317.15
Boiling point (K)	Decomposes	Decomposes
Molecule weight (g/mole)	136.15	200.32
Physical state and appearance	Solid	Solid
Price (USD/kg)	59.00	68.64
Purity	100%	98%

2.3.2 Product

PETD is formed by esterification process between the alcohol group which is the Pentaerythritol and the carboxylic acid which is Lauric Acid or also known as Dodecanoic Acid. The reaction occurs as shown in equation 1:



The non-catalytic reaction occurred at the range 150°C to 230°C. The product was then dried by using water extraction prior to be crystallized at the ambient temperature. The powder was finally obtained by crushing the crystal. The standard material of Pentaerythritol Tetradodecanoate (PETD) is obtained from Kaneka Chemical (M) Sdn. Bhd. The chemicals are those laboratory grades and used without any further purification. Below are some descriptions of the product:

Table 2.2: Physical properties of PETD (*Taken from Kaneka Sdn. Bhd.*)

Properties	Description
Molecular formula	$\text{C}_5\text{H}_8(\text{C}_{11}\text{H}_{22}\text{COOH})_4$
Physical state	Crystalline solid (powder)
Colour	White
Specific gravity	-

Boiling point	-
Melting point	-
Molecular weight	865.372 g/mole

2.4 Chemical Properties of Pentaerythritol Tetradodecanoic (PETD)

The analysis of Pentaerythritol Tetradodecanoate (PETD) is done based quantitative analysis which can be further split into different areas of study. For quantitative analysis, the material can be analyzed for the amount of an element, or for the amount of an element in a specific chemical species.

2.4.1 Thermal Stability

The thermal stability of a pure organic compound is roughly spoken a combination of the thermodynamic and the kinetic stability of a molecule. The addition of other compounds or impurities can effect higher or lower stabilities, in most cases as a consequence of kinetic effects: the added compound (or impurities that could not be removed during the synthesis-procedure) can prevent or open reaction pathways leading to the effects of opposite directions: an advanced stability or an elevated decomposition.

The key parameters for a general view on thermal stabilities with regard to technical applications are:

- i. maximum operating temperature, below which degradation and thus production and evolution of volatile degradants are negligible,
- ii. the rate of degradation at a specific temperature,
- iii. the identification of the decomposition products.

Thermal stability of the Pentaerythritol Tetradodecanoate should be in excess of processing or use temperatures. The thermal stability range can be determined after analyzing the graph of weight percentage remaining versus time.

2.4.2 Melting Point

A melting point is the temperature at which a solid becomes a liquid at normal atmospheric pressure [9]. Determining the melting point of a compound is one way to test if the substance is pure. A pure substance generally has a melting range (the difference between the temperature where the sample starts to melt and the temperature where melting is complete) of one or two degrees. Impurities tend to depress and broaden the melting range so the purified sample should have a higher and smaller melting range than the original, impure sample.

2.4.3 Product Purity

Purchasers of raw products became more demanding about the quality and purity of the product they were purchasing. This means that information about purity and quality of the product flows downstream and that information coming from consumer demand flows upstream [22]. Quality standards are enforced by private commitment to industry standards, as the product value is greater given higher purity levels. Standards enforcement is crucial, as products that do not conform to the desired quality level will not be accepted. Tolerance levels vary from product to product and also depend on the preferences of the final consumer. Testing and tolerance levels are important to ensure that the purity and the high quality levels of the product are maintained. Through purity and product control, it enhances the demand of product hence giving ideal competition to gain customer.

2.4.4 Heat Capacity

Heat capacity is mathematically defined as the ratio of a small amount of heat δQ added to the body, to the corresponding small increase in its temperature dT :

$$C = \left(\frac{\partial Q}{\partial T} \right)_{cond.} = T \left(\frac{dS}{dT} \right)_{cond.}$$

Where δQ is the infinitesimal amount of heat added, and dT is the subsequent rise in temperature.

The heat capacity at constant volume is

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

$$dU = C_V dT$$

$$\Delta U = \int_{T_1}^{T_2} C_V dT$$

And the heat capacity at constant pressure is

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

$$dH = C_P dT$$

$$\Delta H = \int_{T_1}^{T_2} C_P dT$$

2.4.5 Enthalpy

Enthalpy, H can be defined as the sum of the internal energy of the system plus the product of the pressure of the gas in the system and its volume:

$$H_{sys} = E_{sys} + PV$$

After a series of rearrangements, and if pressure is kept constant, we can arrive at the following equation:

$$\Delta H_{sys} = q \quad (\text{at constant pressure})$$

where ΔH is the H_{final} minus $H_{initial}$ and q is heat

The enthalpy is defined by $H = U + PV$. The increment of enthalpy is

$$dH = TdS + VdP$$

2.4.6 Heat of Combustion

Since the calorimeter is isolated from the rest of the universe, we can define the reactants (sample and oxygen) to be the system and the rest of the calorimeter (bomb and water) to be the surroundings. The change in internal energy of the reactants upon combustion can be calculated from

$$\begin{aligned} dU_{tot} &= dU_{sys} + dU_{surr} = 0 \\ dU_{sys} &= -dU_{surr} \\ dU_{sys} &= -\left[\left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV \right] \end{aligned}$$

Since the process is constant volume, $dV=0$. Thus, recognizing the definition of heat capacity C_V yields

$$dU_{sys} = -C_V dT$$

Assuming C_V to be independent of T over small temperature ranges, this expression can be integrated to give

$$\Delta U = -C_V \Delta T$$

where C_V is the heat capacity of the surroundings, *i.e.*, the water and the bomb.

By definition of enthalpy

$$\Delta H = \Delta U + \Delta(pV)$$

Since there is very little expansion work done by condensed phases, $\Delta(pV) \approx 0$ for solids and liquids. Assuming the gas to be ideal yields

$$\Delta H = \Delta U + RT\Delta n_{\text{gas}}$$

Recall that $\Delta U = q_v$ is the heat flow under constant volume conditions, whereas $\Delta H = q_p$ is the heat flow under constant pressure conditions. The difference between these two situations is that pV work can be done under constant pressure conditions, whereas no pV work is done under constant volume conditions.

Consider the case where $\Delta n_{\text{gas}} > 0$, *i.e.*, the system expands during the reaction. The same amount of energy is released by the reaction under both sets of conditions. However, some of the energy is released in the form of work at constant pressure; thus, the heat released will be less than at constant volume. Mathematically,

$$\begin{aligned} \text{heat released} &< \text{energy released} \\ -\Delta H &< -\Delta U \\ \Delta H &> \Delta U \end{aligned}$$

In the case where $\Delta n_{\text{gas}} < 0$, *i.e.*, the system contracts during the reaction, the surroundings do work on the system. Thus, this work is available for energy release from the system back to the surroundings in the form of heat. Mathematically,

$$\begin{aligned} \text{heat released} &> \text{energy released} \\ -\Delta H &> -\Delta U \\ \Delta H &< \Delta U \end{aligned}$$

Enthalpy of a reaction or energy change of a reaction ΔH , is the amount of energy or heat absorbed in a reaction. If the energy is required, ΔH is positive, and if energy is released, the ΔH , is negative.